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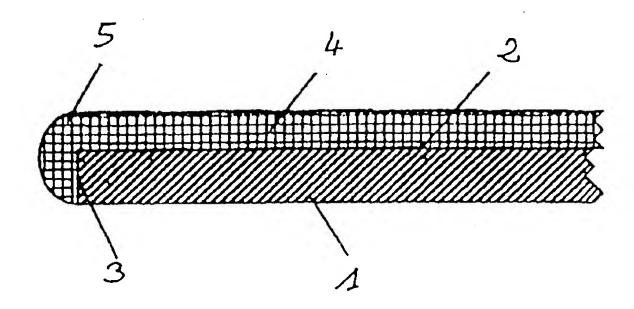
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(54) Titre: SUBSTRATS CONSTITUES DE PELLICULE DE VERRE MINCE, REVETUS DE POLYMERE

(54) Title: POLYMER-COATED THIN-GLASS FILM SUBSTRATES



(57) Abrégé/Abstract:

The invention relates to a glass-plastic composite film and a method for producing same. Conventional glass-plastic composite films are tailored specifically to the requirements of their intended use. The invention aims to create a new composite film which can be used in as wide a range of applications as possibly and is uncomplicated to produce. To this end a glass-plastic composite film is coated with a liquid phase polymer without the use of adhesive. Such a film is characterized by a high-quality surface finish and low optical retardation. It is particularly suitable for the production of illuminated displays on the basis of liquid crystals or light-emitting layers.





# Polymer-coated thin glass film substrates

## Description

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The invention relates to a glass/plastic composite film, in particular for use in electronic components and devices, e.g. displays, made of a glass film having a thickness of between 10  $\mu$ m and 500  $\mu$ m and a polymer layer applied directly to at least one of its side surfaces, which polymer layer has a thickness of between 1  $\mu$ m and 200  $\mu$ m. The invention further relates to a method for producing said glass/plastic composite film and its use.

Flat glass substrates are suitable in many applications as a useful substrate material where transparency, high chemical and thermal endurance and defined chemical and physical properties are required. These are in particular fields of application in which the methods of thin-film and thick-film technology are used such as in displays, thin-film and thick-film sensors, solar cells, micro-mechanical components and lithographic masks. The demand for new product functionalities and fields of applications has recently given rise to the need for increasingly thinner and ultra-thin substrates which come with the known favorable properties of glass substrates, but partly also come with new properties such as flexibility. Typical fields of application are electronic applications such as sensors or membrane elements.

Particularly concerning displays such as liquid crystal displays (LCD) for example, there is a trend towards increasingly appealing design requirements which demand new functionalities. These are in particular ultra-thin and particularly light displays for portable pocket devices, flexible displays for devices with rounded housing shapes such as mobile phones or round pencil-shaped devices or also displays for smart cards or pricing signs or displays on sh lives which ar based on organic or anorganic

light-emitting layers, the so-called light emitting organic polymer displays (OLED).

Such displays are usually structured as follows: The core element is a cell for receiving the liquid crystals or also the polymers which is provided with a front and rear plate to which electrodes are applied. In most liquid crystal displays, polarizers are provided next to the front and rear wall of the cell. A reflector plate is applied behind the rear polarizer in reflective displays. In the case of the emitting polymers, the counterelectrodes can also be vacuum metalized directly on the polymer before the display is closed off with the rear plate. To ensure that the display works as well as possible, it needs to be ensured that for example the liquid crystals are allowed to align as uniformly as possible and the pairs of electrodes all have the same distance with respect to one another to the highest possible extent, since distortions or local fluctuations in intensity of the displays will occur. One factor for influencing is the surface quality of the substrates used for producing the individual components.

Preferred substrate materials for the production of the individual components are glass and plastic. The special advantages of glass are that it is chemically and also photochemically inert, optically isotropic, comes with temperature and mechanical stability, and also has a hard surface. However, it has a relatively high density, is brittle and therefore susceptible to breaking. Glass breakage during the production process leads to losses for the producer not only due to the high number of rejects, but also due to the fact that the process needs to be interrupted in order to clean the machine from any slivers of glass.

Plastic materials have a lower density and are elastic and break-proof, but com with various disadvantages. In the last years substrate materials were developed and produced on the basis of high-quality plastic films for the

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production of displays as a substitute for thin glass substrates. All these films require complex special processes during production in order to achieve the required properties. These complex production methods make the substrates considerably more expensive. Moreover, it has been noticed that the despite considerable development efforts, the water and vapor permeability of such substrate films cannot be sufficiently reduced. This leads to the consequence that the quality and the life of LCDs produced from such substrate films are very limited. In the so-called OLEDs, the oxygen diffusing through the film leads to the oxidation of the organic semiconductor layers and the electrodes consisting of base metals and thus also to a reduction in the life of the displays. When using plastic as a display screen, the susceptibility to scratches reduces the life.

Based on the safety glass industry there are efforts to combine the favorable properties of glass with the favorable properties of plastic: In DE-OS 36 15 277 A1 the glass panes are coated with plastic by melting as a protection from broken glass. In DE-OS 31 27 721 A1 plastic panes are described which are coated with glass films as protection from scratches, with the coating being performed under the influence of pressure and/or heat, preferably by using an interposed hot-melt-type adhesive film.

In analogy thereto, several examples are known in the display technology area to combine the properties of glass and plastic. An approach to provide glass with a plastic protective layer is known from the Korean specification KR-A 98-3695. The glass is presumably brought to the desired thickness by etching and the plastic protective layer is to close the pores produced by the etching and to be used as a protection from breaking. The breakage protection function is in particular that the propagation of already existing microcracks is prevented. No further information is provided on the choice of the polyer with the exception of the information that the resin is from the group of the duroplastics. There is also no further

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information provided on how the protective layer is applied. If one takes into account the glass thicknesses commonly used at the time of the application of said specification for use in the production of displays, which at that time was typically between 0.55 mm to 1.1 mm, and the etched glass surface, the glass/plastic composite materials produced there do not meet the current requirements for display applications. KR-A-98-3695 does not provide any information on the thickness of the protective layer.

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Concerning the production of polarizer films, DE-OS 196 06 386 A1 describes an oriented, optically active dyestuff film made of plastic which is applied for mechanical stabilization onto a glass film by pressing, melting and, preferably, gluing. The adhesive is used for an additional mechanical stabilization of the dyestuff film. The glass film thicknesses vary between 10 and 200  $\mu$ m; the dyestuff film thicknesses between 5 and 60  $\mu$ m.

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The application of the dyestuff film is not unproblematic. During the pressing, the number of rejects by glass breakage is very high. Melting is a complex process which can negatively influence the properties of the dyestuff films. Gluing comes with the following disadvantages: The process of gluing of films, which in this case is a polymer film with a glass film, is also known as lamination. The lamination is generally performed by rolling by using pressure. This leads to a considerable stress on the glass film which leads to breakage or damage to the glass film, e.g. scratches on the surface, particularly where very thin films are concerned. At least four separate production processes are necessary, namely the production of the thin glass, the production of the film, the coating with the adhesive and the actual lamination process, which all lead to considerable costs. Moreover, high demands are placed on the gluing and laminating technique, because the product must not contain any air or dust particles, particularly in the case of display applications. In choosing the adhesive it is necessary to consider that they usually only come with a reduced t mp rature and

solvent endurance. A homogeneous thickness of the glass laminate cannot be sufficiently guaranteed due to fluctuations in the thickness in the ductile adhesive layer.

The use of polymer films per se is problematic because they build up considerable compressive and tensile stresses during temperature fluctuations in the laminate due to their high degree of cross-linkage. The thermal coefficients of expansion of plastic are one magnitude higher than that of glass. Moreover, all polymer films show irreversible shrinkage after temperature cycles close to the glass transition temperature, leading to a permanent distortion of the laminates. This effect is frequently inhomogeneous and can be anisotropic in oriented films.

Moreover, polymer films usually show a far from inconsiderable optical retardation (double refraction) which is clearly over 20 nm. An optical anisotropy of the film is not permitted in displays which utilize the double refraction effect of liquid crystals. The lateral double refraction  $\Delta n$  in a film is obtained from the difference of the refractive index parallel and vertical to the process direction of the films. The optical retardation  $\gamma$  of a film with the thickness d is obtained therefrom from the product from the difference of the refractive indexes parallel and vertical to the process direction of the films and the film thickness.

Only substrates or substrate films with an optical retardation of < 20 mm can be used for LCD applications which utilize the double refraction of the liquid crystal. Most drawn films which are obtainable on the market show a multiple of this value, however. Only few films can be obtained that fall below this value. Due to more complex production methods they are very expensive however.

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Another factor in very thin polymer films is that they can be handled only with difficulty in a lamination process and therefore lead to adverse yields. They can be laminated free from warping only with difficulty, which can lead to additional tensions and to the warping of the laminate. Film laminates with a polymer film thickness of  $< 25 \mu m$  can hardly be produced on a major scale and in an economically viable manner.

A plastic substrate is described in the Japanese specification JP-A 4-235527 on which a glass film is applied in order to improve the surface quality of the plastic substrate in such a way that an electrically conducting layer for the attachment of electrodes thereon can be applied. Transparent epoxy resins are preferably used as material for the plastic substrate. The substrate thickness can be 100  $\mu$ m up to 10 mm, depending on the intended application, and especially depending on the surface size of the display to be produced. The thickness of the glass film is between 10  $\mu$ m and 500  $\mu$ m. Either the glass film and the plastic substrate are glued together or the resin is cast onto the glass. The aforementioned problems arise already during the gluing, which can have a negative influence on the optical properties and surface quality of the end product. Moreover, substrate thicknesses of > 100  $\mu$ m come with the disadvantage that the glass/plastic composite films are flexible only within limits.

In all end products presented up until now it is already predetermined by the end product per se which side is further processed and how it can be further processed. In JP-A 4-235527 it is tried for the first time to remedy this by applying a glass film to both sides of the plastic substrate. For this purpose at least one process step is required, and where gluing is concerned at least even two further process steps and more material. It is therefore considerably more laborious to produce an end product whose both sid s are to be further processed.

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From EP 0 838 723 A a material has become known which is provided with a layer on a glass base. This material is suitable for lithographic prints and for liquid crystal displays. The material comprises a glass base which is thinner than 1.2 mm and is resistant to tensile stresses up to and over 5 x 10<sup>7</sup> Pa. Moreover, the edges are arranged in the longitudinal direction semi-circular with a radius of approx. 0.5 times the thickness of the base.

EP 0 272 875 A describes an optical memory card and a method for its production, with the card consisting of plastic and aluminum.

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EP 0 759 565 A describes a method for producing a color filter array element. A colored pattern of pixel cells is applied for this purpose on a thin support which is rigid in the horizontal plane. A transparent support is thereafter laminated either onto the side of the support or the side of the pixel cells, with a thin glass pane (127  $\mu$ m) with polycarbonate being coated at first by spin coating.

After the production of the pixel cells a borosilicate plate is laminated onto the pixel cells under pressure.

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A transparent glass/plastic material composite pane, comprising at least one transparent plastic pane, at least one glass pane and an adhesion-promoting intermediate layer. The glass pane is a glass film of a layer thickness ranging from 30 to 1,000  $\mu$ m. The plastic pane has a thickness of several millimeters, because the composite pane is to be used as light, scratch-proof glazing in vehicles.

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GB 131 98 46 discloses a glass/plastic composite film with a glass film with a thickness of 4 to 200  $\mu$ m which is coated on either one or both surfaces with plastic of a thickness of 2 to 200  $\mu$ m. Production is p rformed either with an adhesiv or a bonding agent. The plastic can also be applied

directly from the liquid phase as an alternative. The plastic materials employed include polyolefines, PVC, PA, polyvinylidene chloride, cellulose, cellulose acetate, polystyrene or also polymer mixtures or copolymers of said polymers. Particularly preferable are polyester or polyethylene terephthalate. The glass/plastic composite film known from GB 131 98 46 is to be used preferably as a film material for drawings or as gas- and vacuum-impermeable packaging material. Accordingly, the optical properties which are important in an application in the area of electronic components are irrelevant in GB 131 98 46 and are not mentioned in this specification.

The later published applications WO 99/21707 and WO 99/21708 describe laminates from a glass substrate and at least one base which can consist of transparent plastic. The glass layer has a thickness of 10 to 450 um and the plastic layer a thickness of  $> 500 \mu m$ . The plastic layer can also be applied onto the glass without plastic by means of vacuum lamination. Continuous rolling is also proposed in this respect. If glue is used nevertheless, it should be thermally stable up to 200°C. In particular in vacuum lamination it is important that both plastic as well glass have a low surface roughness. This is not quantified in further detail. Silicones, acrylates and polymers which can be cross-linked with UV light are proposed as the adhesive layer. A bonding agent such as epoxy hydrosilicone can also be applied onto the glass when a functional layer is to be applied on the glass. The entire laminate can optionally be coated with a sol-gel. Since the laminate is to be used for displays in particular, plastic and glass should be chosen in such a way that they have a refractive index which is as similar as possible.

WO 99/21708 describes a method for producing semiconductor devices in that a functional layer is applied on a substrat, with the substrate concerning a laminate which consists of a base and a glass layer with a

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thickness of less than 700  $\mu$ m. A laminate is substantially concerned as is described in WO 99/21707.

The later published GB 233 58 84 discloses a component for use as a protective element in optoelectronic or electronic components, comprising at least one electrically active organic layer, with the component comprising a glass layer with a thickness of > 200  $\mu$ m and a plastic layer, with the plastic layer having a thickness of > 1 mm, preferably around 200  $\mu$ m. Disadvantageous in GB 233 58 84 is the processing of the active organic functional layer which requires a complex process.

It is the object of the present invention to provide a film which can be used as widely as possible, in particular in the production of displays as a basis for the production of all components such as the liquid crystal cell, the cell for receiving the light-emitting layer in OLEDs or also the electrode layer. It should not only meet the current but also the future demands placed on the film quality and have the advantageous properties of both glass and plastic. The production method should make do with only a few steps and be as uncomplicated as possible.

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This object is achieved by a glass/plastic composite film which is characterized in that in a glass/plastic composite film in accordance with the preamble the polymer layer is applied directly to at least one side surface in order to avoid the disadvantages of lamination in particular.

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It is of particular advantage for use in the field of electronic components and devices when at least one lateral surface is provided on its surface with a waviness of less than 100 nm and/or a roughness  $R_{\rm T}$  of > 30 nm, and/or that the optical retardation is not more than 20 nm. A particularly flexible composite is obtained when the thickness of the applied polymer layer is in the range between 1  $\mu$ m and 100  $\mu$ m.

This object is moreover achieved by the two following methods:

The first method comprises the steps of producing a glass film with a thickness of 10 to 100  $\mu$ m in the down-drawn process with a drawing speed of 2 to 12 m/s, pretreatment of the glass film surface, direct application of a polymer layer of 1 to 200  $\mu$ m thickness in the liquid phase and serializing the polymer-coated glass film.

The second method comprises the same steps, with the glass film being serialized already after the production and prior to the pretreatment of its surface and the application of the plastic.

In contrast to the known lamination methods it is possible by this method to produce very thin and homogeneous polymer films on the glass film.

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The glass/plastic composite film in accordance with the invention is suitable in the case of the production of displays and due to its high surface quality both for further processing into a polarizer film and into a base plate for electrodes as well as for use as the outermost protective pane. The film is resistant to breakage and at the same time lighter due to the plastic layer. As a result of the glass film layer it is scratch-proof, hard, mechanically stable and chemically inert. Depending on whether the glass side or the plastic side is further processed, either the plastic side is used as breakage protection or the glass side as protection from scratching. As a result of the low double refraction, the glass/plastic composite film in accordance with the invention is particularly suitable for use in optoelectronic components and devices. The high surface quality of the composite film is particularly relevant for the production of liquid crystal cells and luminous displays on the basis of light-emitting layers. Rough surfaces can lead to defective spots in the display because rough surfaces can easily lead to a heterog neous alignment of the liquid crystals in the applied orientation

layers. Waviness leads to fluctuations in the layer thickness in the active layer (e.g. liquid crystal) and thus to an inhomogeneous display.

The roughness  $R_{T}$ , which is also known as surface roughness, is determined according to DIN 4762 Part 1-08.60. and corresponds to the maximum distance between profile peak and profile valley within a reference section. It should not be confused with roughness  $R_A$  which corresponds to the arithmetic means of all distances and is usually only a fraction of  $R_T$ . The roughness describes the short-wave share of the deviation from an ideal plane surface, whereas waviness (measured according to DIN/ISO 11562 with a cut-off of 0.8 to 8.0 mm and 2CRPC 50 filters) covers the deviation of the mean wavelength.

In a particularly preferable embodiment both sides of the glass/plastic composite film comprise the high surface quality of a waviness of less than 100 nm and a roughness  $R_T$  of less than 30 nm. As a result, the glass/plastic composite film can be used even more universally because it can be further processed similarly on both sides and also opens the possibility to further process it on both sides.

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In order to obtain the lightest and thinnest possible glass/plastic composite film which is provided with the highest surface quality, it is mandatory that it is actually only composed of the polymer and the glass film and does not comprise any adhesive layer.

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Particularly in the area of optoelectronic applications the optical retardation is advantageously  $\leq$  20 nm, preferably  $\leq$  15 nm, in order to suppress any distortion of the optical signals by the composite film.

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In view of the reduction of the weight and the thickness of the display, the glass film layers preferably have a thickness of 10 to 400  $\mu$ m, more

preferably 10 to 200  $\mu$ m and especially preferably 10 to 100  $\mu$ m, and the polymer layer preferably 2 to 100  $\mu$ m and particularly preferably 2 to 50  $\mu$ m, and the optical retardation is not more than 15 nm.

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Since a large portion of the glass breakage in glass films are caused by microcracks which start at the edges, it is advantageous that at least one edge of the glass/plastic composite film is entirely covered by plastic. This prevents the origination of new cracks as well as the propagation of already existing cracks.

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In order to make the glass/plastic composite film less susceptible to punctiform loads, it has proven to be advantageous to choose the polymers for the plastic layer in such a way that its modulus of elasticity is < 5,000 N/mm², preferably < 2,600 N/mm², and more preferably < 1,500 N/mm². The occurring tensile load is distributed by the polymer layer over a larger surface area and is thus substantially reduced.

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The modulus of elasticity of a very thin plastic layer can be determined from force penetration depth measurements. For this purpose a test piece of defined geometry, which is usually a pyramidally ground diamond, is pressed into the surface with a growing load and thereafter relieved again. The modulus of elasticity is obtained from the increase of the straight relief line (penetration depth depending on the load). The measurements are performed with a so-called pico indentor, with which it is possible to perform very small penetration depths of between 10 and 100 nm. This is necessary because when the penetration depth exceeds approx. 10% of the layer depth the substrate begins to influence the measurement.

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It has proven to be particularly advantageous to choose a polymer for the plastic layer in such a way that the transmission of the glass/plastic composite film is more than 90% of the uncoated glass film and the

haziness caused by the polymer coating increases by less than 1% as compared with the uncoated glass film.

In order to have the as many possibilities as possible for the further processing of the glass/plastic composite film and to ensure a high service life of the products produced on the basis of the glass/plastic composite film, the glass/plastic composite film is preferably permanently temperature stable up to 130°C (over several hours), and up to 140°C, preferably up to 180°C, and especially preferably up to 200°C, short-term temperature stable (a few minutes).

Glass/plastic composite films have proven to be particularly advantageous for the production of LCD and OLED displays which are provided on its surfaces with a roughness  $R_T$  of < 10 nm, particularly preferably < 3 nm, and a waviness of < 80 nm.

Preferred materials to obtain optimal glass/plastic composite films are silicone polymer, sol-gel polymer, polycarbonate, polyether sulphone, polyacrylate, polyimide, cyclo olefin copolymer or polyarylate for the plastic layer and borosilicate glass preferably alkali-free borosilicate, for the glass layer.

In order to produce a glass/plastic composite film it is necessary to produce the glass film per se. In order to produce a glass film of the required surface quality the down-draw process should be used with drawing speeds of between 2 and 12 m/s. The surface quality of the glass film is the prerequisite for the achievement of a respective surface quality on the plastic side of the glass/plastic composite film. After the production of the glass film the same can either be further treated directly or, if the steps of pretreating th glass film surfac and the application of the polymer lay r are spatially separated from the glass film production, can be

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serialized at first, which is preferable in the production of smaller or medium quantities. The pretreatment of the glass film surface is performed in order to ensure a favorable adherence of the polymer layer.

As a result of the direct application of a polymer on the glass film surface without adhesive, namely in the liquid phase, it is achieved that the surface of the polymer layer virtually reproduces the surface of the glass film and shows its outstanding surface quality. If the production of the glass film and the pretreatment and the coating are planned as a continuous process, the polymer-coated glass film is now serialized.

As a result of the application of the liquid phase on the rigid glass film it is also ensured that no direction of warping is formed in the polymer film and thus the optical retardation of the polymer film and, consequently, the composite film is less than 20 nm.

If the glass film has been serialized prior to the coating and if one wishes to obtain extremely thin polymer layers, the coating preferably occurs by spinning or spray spinning. Coating methods which are also suitable for a continuous process are casting, rolling or spraying. Dipping is the preferable method for applying the polymer layer to both side surfaces of the glass film.

In order to increase the resistance to fractures, at least one edge of the film should be co-coated simultaneously. In the continuous process the edges are coated parallel to the drawing direction. All four edges can be coated in senalized pieces of film.

Advantageous with respect to the properties of the glass/plastic composite film ar th us of glass films of 10 to 400  $\mu$ m, preferably 10 to 200 mm and particularly preferably 10 to 100  $\mu$ m, and the application of polymer

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layers of 1 to 200  $\mu$ m, preferably 2 to 100  $\mu$ m and particularly preferable 10 to 85  $\mu$ m.

In order to increase the bonding of the polymer layer on the glass film, best results are obtained by surface treatment by UV radiation of the glass film surface in an ozonic atmosphere, by corona treatment or by flaming.

The film should be radiated with ultraviolet light and/or dried under the influence of heat to support the curing of the polymer layer.

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Glass/plastic composite films with particularly favorable properties are obtained when either silicone polymer or sol-gel polymer or polycarbonate or polyether sulphone or polyacrylate or polyimide, cyclo olefin copolymer or a polyarylate are used as polymer. For this method, the use of borosilicate glass, preferably alkali-free borosilicate glass, is particularly advantageous for the production of the glass film.

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Included in the protection are also to be the connection of the glass/plastic composite film in accordance with the invention to produce electronic components and optoelectronic devices, in particular on the basis of liquid crystals or light-emitting layers.

The invention is to be explained in closer detail by reference to the embodiments shown in the enclosed drawings, wherein:

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- Fig. 1 shows a sectional view through the glass/plastic composite film at an edge, and
- Fig. 2 shows a production line for producing the glass/plastic composite film.

Fig. 1 shows a sectional view through the glass/plastic composite film at one of its edges. A polymer film 4 is applied on a glass film 1 directly on the glass film surface 2. Said polymer film 4 extends beyond the glass edge 3 and therefore forms an edge bead 5 which completely covers the glass edge 3. In this way the edge of the glass/plastic composite film is protected from impact shocks and a propagation of microfractures that may exist in the edge is prevented there.

Fig. 2 shows a possible production line for producing the glass/plastic composite film. In the glass production line 10 the glass film 15 is produced in the so-called modified down-draw method by drawing the glass film 15 in a hot-forming step vertically from the glass tank 11 and the debiteuse 12 and optionally re-forming it on the cooling stretch 13. As a result of the direct coupling of the feeding path, a minimal contamination and change to the surface of the glass prior to the subsequent coating is obtained, which is particularly favorable for the bonding capability of the polymer layer. As a result of a minimum number of treatment, transport and intermediate storage steps, the production of surface injuries and contamination with particles is kept to a minimum. In order to compensate any adjustment to the process speed and tolerances, if any, a buffer stretch 16 in form of a loop is provided after the glass production line 10, thus achieving a separation between glass drawing and coating process. As a result of the substantially free suspension of the glass film 15 any impermissible warping of the glass 15 which could lead to tearing and soiling of the glass surface are prevented.

The glass film 15 is guided in the further progress horizontally via conveying rollers 20 and regulated via traction rollers 21 in their tractive force in order to insure an evin conveying speed and tractive force and to prevent any tearing off of this glass film 15. The surface to bicoated is treated in the surface treatment unit 22 by UV radiation in an ozonic

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atmosphere. In order to set the required glass temperature prior to the application of the polymer, a tempering unit 23 is disposed before the coating module 24 which preheats the glass ribbon to a precisely defined homogeneous temperature. The application of the coating occurs by the coating module 24. The polymer 25 flows through the sheet die 26 onto the transfer roller 27 is rolled onto the glass film by applying minimal pressure (< 1 kg/cm<sup>2</sup>). In the first drying line 28 the solvent for evaporation is applied. The evaporated solvent is recycled to the process after treatment and cleaning in order to reduce any pollution to the environment and consumption per se. An increased temperature of the glass film 15 leads to a rapid evaporation of the solvent without the formation of any dry skin on the surface which would prevent any evaporation of the solvent enclosed in the volume. The curing and drying of the polymer layer occurs in the UV exposure line 30 and the second drying line 31. At the end of the line there is a winding unit 33 with intermediate layer unwinder 32 from which an intermediate layer is wound up between the glass/plastic composite film layers. Thereafter the glass/plastic composite film roll is brought to the serialization plant.

#### 20 Embodiment 1

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Production of a glass/polysilicone composite 100  $\mu$ m/40  $\mu$ m by roller coating

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A glass film made of borosilicate glass of glass type D 263 (maker's legend: Schott-DESAG) with a thickness of 100  $\mu$ m which is produced with the glass drawing process known as down-draw at a drawing speed of the glass ribbon of 5.5 m per min. The surface of the glass substrate has a waviness of 60 nm and a roughness R<sub>T</sub> of 9 nm. The surface of the glass ribbon is activated by a corona treatment. The multi-knife metal electrode has a width of 500 mm and the distance of the lectrod to the glass

surface is 2 mm. The frequency is 30 to 50 kHz (automatic frequency control) and the output 150 W. The two-component silicone polymer film on the basis of polydimethyl siloxane which is applied with a roller coating method (product name: Elastosil, mixture ratio of both silicone components: 9:1) has a thickness of 40  $\mu$ m. The roller diameter is 238 mm and the roller length 550 mm at a mean pressing pressure of 0.5 kg/cm². In a subsequent tempering process the silicone-coated glass ribbon is cured at 150°C for 10 mins. and thereafter serialized. The modulus of elasticity of the silicone layer is 1100 N/ cm² and the surface has a waviness of 50 nm and a roughness of 20 nm. As a result of the roller coating, the lateral edges disposed parallel to the direction of rolling are covered with the silicone polymer. The optical retardation is 15 nm.

#### **Embodiment 2**

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Production of a glass/polysilicone composite 50  $\mu$ m/2  $\mu$ m by the spinning method

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A glass film is used from an alkali-free borosilicate glass AF 45 (maker's legend: Schott-DESAG) with a film thickness of 50  $\mu$ m, a waviness of 80 nm and a roughness R<sub>T</sub> of 4 nm which is produced in the down-draw process with a drawing speed of 10 m per min. The film size is 300x200 mm². The glass substrate is cleaned by a washing process and thereafter activated for 5 minutes by a UV ozone treatment (amalgam low-pressure radiator, 500 W) at 184.9 nm for the formation of ozone and at 253.7 nm for the formation of oxygen radicals on the surface. With a spinning process (speed of 2,400 1/min) the glass film is coated with a single-component polydimethyl silicone (dissolved in hexane with a mass ratio of polymer and hexane of 1:21) and dried thereafter at 120°C for 15 mins. in a forced-air oven. The layer thickness is 2  $\mu$ m. All four side edges are covered with silicon polymer as a result of the spin coating. The modulus of lasticity of

the silicone layer is 500 N/mm $^2$  and the surface has a waviness of 67 nm and a roughness R $_{\rm T}$  of 9 nm. Optical retardation is 5 nm.

#### **Embodiment 3**

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D 263 glass/polycarbonate composite 145  $\mu$ m/3  $\mu$ m with the spinning method

A glass film of glass type D 263 (maker's legend: Schott-DESAG) as glass substrate with a thickness of 145  $\mu$ m is used. It is produced in the downdraw process with a drawing speed of 4.2 m/min. Waviness is 28 nm, roughness R<sub>T</sub> is 8 nm. The glass substrate is cleaned by a washing process and thereafter activated for 5 minutes by a UV ozone treatment (amalgam low-pressure radiator, 1,000 W) at 184.9 nm for the formation of ozone and at 253.7 nm for the formation of oxygen radicals on the surface. With a spinning process (speed of 1,400 1/min) the glass film is coated with a polycarbonate film (polycarbonate/methylene chloride solution, mass ratio 1:19) and dried thereafter at 80°C for 20 mins. in a forced-air oven. The layer thickness is 3  $\mu$ m. All four side edges are covered with polycarbonate film. The modulus of elasticity of the polycarbonate layer is 1350 N/mm² and the surface has a waviness of 30 nm and a roughness R<sub>T</sub> of 9 nm. Optical retardation is 9 nm.

#### **Embodiment 4**

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AF 45 glass/polyether sulphone (PES) 200  $\mu$ m/85  $\mu$ m by extrusion method

A glass film of an alkali-free borosilicate AF 45 (maker's legend: Schott-DESAG) with a film thickness of 200  $\mu$ m is used. The surface of the glass substrate has a waviness of 55 nm and a roughness (R<sub>T</sub>) of 7 nm. The drawing speed of the glass ribbon is 2.8 m/min.

The surface of the glass ribbon is activated by a corona treatment. The stick electrode has a width of 500 mm and the distance of the electrode from the glass surface is 4.5 mm. The frequency is 30 to 50 kHz (automatic frequency control) and the output 250 W. The PES film which is applied with an extrusion method at a drawing speed of 2.8 m/min at 380°C has a thickness of 85  $\mu$ m. The glass/PES composite is serialized after a cooling-off period of 5 mins. The modulus of elasticity of the PES layer is 3,200 N/cm² and the surface has a waviness of 68 nm and a roughness R<sub>T</sub> of 15 nm. As a result of the extrusion coating, the lateral edges disposed parallel to the direction of extrusion are covered with the PES polymer. The optical retardation is 18 nm.

#### **Embodiment 5**

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AF 45 glass/polyacrylate composite 50  $\mu$ m/10  $\mu$ m by spray coating

A glass film is used from an alkali-free borosilicate glass AF 45 (maker's legend: Schott-DESAG) with a film thickness of 50  $\mu$ m, a waviness of 80 nm and a roughness R<sub>T</sub> of 4 nm which is produced in the down-draw process with a drawing speed of 10 m per min. The film size is 300x200 mm². The glass substrate is cleaned by a washing process and thereafter activated for 5 minutes by a UV ozone treatment (amalgam low-pressure radiator, 500 W) at 184.9 nm for the formation of ozone and at 253.7 nm for the formation of oxygen radicals on the surface. The polyacrylate layer with a thickness of 10  $\mu$ m is produced by a spray method with an acrylate aerosol. All four side edges are covered with the polymer. The High Pressure Low Volume (HPLV) method is used as the spray method. The 10% polyacrylate solution in N,N-dimethyl formamide which is preheated to 40°C is sprayed via a spray nozzle with a diameter of 0.6 mm, with the spray pressure being at 0.55 bar and the feding pressure of the nozzle being at 4 bar. The modulus of elasticity of the acrylate layer is 5,000

 $\rm N/mm^2$  and the surface has a waviness of 75 nm and a roughness  $\rm R_T$  of 10 nm. Optical retardation is 8 nm.

## **Embodiment 6**

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D 263 glass/cyclo-olefine copolymer (COC)

A glass film is used as glass substrate which is made of glass type D 263 (maker's legend: Schott-DESAG) with a thickness of 145  $\mu$ m which is produced with the down-draw process, with the waviness being 28 nm and the roughness R<sub>T</sub> 8 nm. The surface of the glass ribbon is activated by a corona treatment. Three multi-knife metal electrodes which are disposed behind one another each have a width of 500 mm and a distance to the glass surface of 7 mm. The frequency is 30 to 50 kHz (automatic frequency variation) and the output is 120 W per metal electrode. The drawing speed of the glass film is 4.2 m/min. The COC film with a thickness of 15  $\mu$ m is applied with an extrusion method at 4.2 m/min at 270°C, with the glass edges which are parallel to the drawing direction being covered with the polymer. After a cooling-off period of 7 min the coated glass ribbon is serialized. The surface has a waviness of 26 nm and a roughness R<sub>T</sub> of 15 nm. The modulus of elasticity is 2,800 N/mm². The optical retardation is 10 nm.

#### Embodiment 7

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D 263 glass/polyarylate composite 145  $\mu$ m/3.5  $\mu$ m by dipping

A glass film is used as glass substrate which is made of glass type D 263 (maker's legend: Schott-DESAG) with a thickness of 145  $\mu$ m which is produced with the down-draw process, with the waviness being 28 nm and the roughness R<sub>T</sub> 8 nm. The glass substrated size is 200x200 mm<sup>2</sup>. The

glass substrate is cleaned by a washing process and thereafter activated for 5 minutes by a UV ozone treatment (amalgam low-pressure radiator, 1,000 W) at 184.9 nm for the formation of ozone and at 253.7 nm for the formation of oxygen radicals on the surface. The polyarylate is predried in a furnace at 130°C and sodium-dried toluol is used as a solvent. The polyarylate with a thickness of 35  $\mu$ m is applied in a dipping process (polyarylate/toluol; mass ratio 1:18, process temperature 80°C) under nitrogen atmosphere, and dried with subsequent tempering process at 160°C for 10 min. All four side edges are covered with the 3.5  $\mu$ m thick polyarylate film. The modulus of elasticity is 2,400 N/mm² and the surface has a waviness of 19 nm and a roughness R<sub>T</sub> of 10 nm. Optical retardation is 8 nm.

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# Reference numerals

Glass film

5 Glass film surface

Glass edge

Polymer film

Bead edge

Glass production line

10 Glass tank

Debiteuse

Cooling line

Rollers

Glass film

15 Buffer line

Conveyor rollers

Rollers

Surface treatment unit

Tempering unit

20 Coating module

Polymer

Sheet die

Transfer roller

First drying line

25 Suction system

UV exposure line

Second drying line

Intermediate layer unwinder

Winding unit

# Enclosure of the International Pr Ilminary Examination R port

### CLAIMS:

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- 1. A glass/plastic composite film, in particular for use in electronic components and devices such as displays, made of a glass film having a thickness of between 10 μm and 500 μm and a polymer layer applied on at least one of its side surfaces with a thickness of between 1 μm and 200 μm, especially between 1 μm and 100 μm, with the polymer layer being applied directly to at least one side surface, characterized in that on at least one side the optical retardation is not more than 20 nm.
- 15 2. A glass/plastic composite film as claimed in claim 1, characterized in that at least one side on its surface shows a waviness of less than 100 nm.
- 3. A glass/plastic composite film as claimed in claim 2, characterized in that at least one side shows a roughness  $R_T > 30$  nm.
  - 4. A glass/plastic composite film as claimed in one of the claims 1 to 3, characterized in that both sides show on their surface a waviness of less than 100 nm and a roughness R<sub>T</sub> of less than 30 nm.

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5. A glass/plastic composite film as claimed in one of the claims 1 to 4, characterized in that the glass thickness is 10 to 400  $\mu$ m, preferably 10 to 200  $\mu$ m and more preferably 10 to 100  $\mu$ m.

- 6. A glass/plastic composit film as claimed in on of th claims 1 to 5, characterized in that the thickness of the polymer layer is 2 to 100  $\mu$ m, preferably 2 to 50  $\mu$ m.
- A glass/plastic composite film as claimed in one of the claims 1 to 6, characterized in that the film also comprises the polymer layer on at least one edge.
- 8. A glass/plastic composite film as claimed in one of the claims 1 to 7, characterized in that the polymer layer has a modulus of elasticity of < 5,000 N/mm², preferably of < 2,600 N/mm² and more preferably of < 1,500 N/mm².
  - 9. A glass/plastic composite film as claimed in one of the claims 1 to 8, characterized in that the transmission of the glass/plastic composite film is more than 90% of the uncoated glass film and the haziness caused by the polymer coating increases by less than 1%.
- 10. A glass/plastic composite film as claimed in one of the claims 1 to 9,
   20 characterized in that the roughness of the surface is R<sub>T</sub> ≤ 20 nm,
   preferably ≤ 10 nm, the waviness of the surface is ≤ 80 nm,
   preferably ≤ 50 nm, and the optical retardation is not more than 15 nm.
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  11. A glass/plastic composite film as claimed in one of the claims 1 to 10, characterized in that in permanent use the film is temperature-stable up to 130°, and up to 140°C in the case of short-term heating, preferably 180°C, more preferably 200°C.
- 30 12. A glass/plastic composite film as claimed in one of the claims 1 to 11, characterized in that the polymer layer consists of a silicon

polymer, a sol-gel polymer, a polycarbonate, a polyether sulphone, a polyacrylate, a polyimide, a cyclo-olefine polymer or a polyarylate.

- 13. A glass/plastic composite film as claimed in one of the claims 1 to 12, characterized in that the glass film consists of a borosilicate glass, preferably an alkali-free borosilicate glass.
- 14. A method for producing a glass/plastic composite film as claimed in one of the claims 1 to 13, with the following steps:
  - the production of a glass film of a thickness of 10 to 500  $\mu m$  in the down-draw process with a drawing speed of 2 to 12 m/s;
  - pretreatment of the glass film surface;
  - direct application of a polymer layer with a thickness of 1 to 200  $\mu m$  in the liquid phase;
  - serialization of the polymer-coated glass film.
- 15. A method for producing a glass/plastic composite film as claimed in one of the claims 1 to 14, with the following steps:
  - the production of a glass film of a thickness of 10 to 500  $\mu m$  in the down-draw process with a drawing speed of 2 to 12 m/s;
  - serialization of the glass film;
  - pretreatment of the glass film surface;
  - direct application of a polymer layer with a thickness of 1 to 200  $\mu m$  in the liquid phase.

16. A method as claimed in claim 15, characterized in that the application of the polymer layer is performed by spinning or by spray spinning.

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- 17. A method as claimed in claim 14 or 15, characterized in that the application of the polymer layer is performed by casting or rolling or spraying or dipping.
- 5 18. A method as claimed in one of the claims 14 to 17, characterized in that at least one edge is coated in addition to the side surface.
  - 19. A method as claimed in one of the claims 14 to 18, characterized in that a glass film is produced with a thickness of 10 to 400  $\mu$ m, preferably 10 to 200  $\mu$ m, more preferably 10 to 100  $\mu$ m, in the glass production line in the down-draw process.
  - 20. A method as claimed in one of the claims 14 to 19, characterized in that the coating leads to a polymer layer thickness of 2 to 100  $\mu$ m, preferably 2 to 50  $\mu$ m.
  - 21. A method as claimed in one of the claims 14 to 20, characterized in that the surface treatment is performed before the coating as UV radiation in an ozonic atmosphere or as a corona treatment or as flaming.
  - 22. A method as claimed in one of the claims 14 to 21, characterized in that after the coating, the polymer coating is cured with the help of UV radiation and/or is dried under the influence of heat.
  - 23. A method as claimed in one of the claims 14 to 22, characterized in that a silicone polymer, a sol-gel polymer, a polycarbonate, a polyether sulphone, a polyacrylate, a polyimide, a cyclo-olefine copolymer or a polyarylate are applied as a polymer.

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24. A method as claimed in one of the claims 14 to 23, characterized in that a borosilicate glass, preferably an alkali-free borosilicate glass, is used for the production of the glass film.

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The application of the glass/plastic composite film as claimed in one of the claims 1 to 13 for the production of electronic components and optoelectronic devices, in particular on the basis of liquid crystals or light-emitting layers.

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